CHAPTER 5

5. ONE-DIMENSIONAL CLUSTERS OF UREA AND THIOUREA

This chapter describes *ab initio* and semiempirical molecular orbital calculations on one-dimensional hydrogen-bonding aggregates of urea and thiourea corresponding to the two patterns: chains and ribbons. We will also consider transverse chains, obtained from ribbons by 90° rotation of every other molecule about the C=O bond. All of these aggregates are found in the crystal structures of these molecules. Ribbons are primary agglomerates in orthogonal structure (**CAB** on Figure 3.5), while chains are primary agglomerates in tetragonal structure (**CAB** on Figure 3.4). Transverse chains are orthogonal to the chains in tetragonal crystal structure (**DAE** on Figure 3.4) and are related to ribbons by rotation of all odd molecules perpendicular to the ribbon plane. As we described in Chapter 4, ribbons are formed by cyclic dimers, the most stable for urea. Chains are formed by head-to-tail dimers, the next stable type. Transverse chains are formed by herringbone dimers, the least stable for urea.

In the previous chapter we have shown that equilibrium geometry of the urea molecule is not planar at all levels of theory. The barrier to planarization is systematically lowered by increasing size of the basis set, H-bond formation and application of external electric fields. Moreover, zero-point vibrational energy corrections make the planar structure of the isolated molecule preferable at the Hartree-Fock, Møller-Plesset and density functional theory levels using the large 6-311+G(3df,2p) basis set. Based on these results, we considered the urea molecule to be planar for all aggregates considered. The thiourea molecule, which is even more

easily planarized, was also held planar in the aggregates calculated.

5.1 Method

Theoretical calculations were performed using the GAUSSIAN 94/98 programs for both *ab initio* and semiempirical molecular orbital (MO) methods. Unless otherwise noted, all geometries were optimized with the following constraints: (a) all molecules are assumed to have C_{2v} symmetry; (b) inter- and intramolecular geometrical parameters were kept equivalent for molecules within a given aggregate. These constraints are meant to simulate translational symmetry within the crystal. Full optimization was performed in some cases for comparison.

Periodic HF calculations on infinite chains and ribbons were performed using the CRYSTAL 92/95 programs. We used single-point energy calculations on the optimized geometry of the decamer.

Since the result of partial optimization is not a stationary point, vibrational frequencies were calculated for fully optimized oligomers only. These were used to estimate ZPVE corrections for other oligomers. We performed HF, DFT and MP2(frozen core) calculations using the D95** basis set, as well as AM1 semiempirical calculations. For the DFT calculations, we used the hybrid B3PW91.

5.2 Energy of the last H-bond and errors due to constraints and finite cluster size

We have considered the primary one-dimensional agglomerates in tetragonal and orthogonal crystal structures: planar chains and ribbons (Figure 5.1). The energies
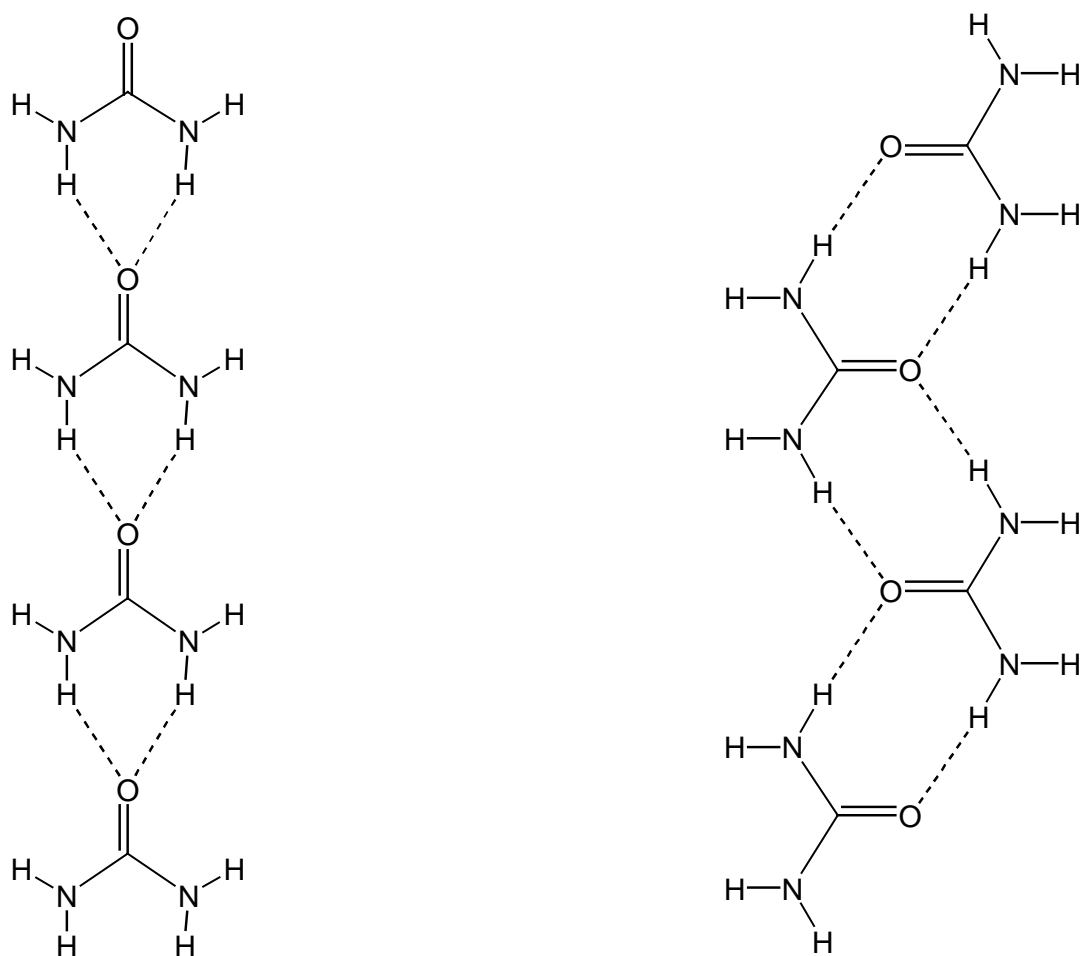
Figure 5.1. Hydrogen-bonding patterns in chains (left) and ribbons (right) of urea. The structures for thiourea are analogous.

obtained for these oligomers at the HF/D95** level are presented in Table 5.1. The geometrical parameters are summarized in Table 5.2. As one can see from Table 5.1, the net stabilization energy, ΔE, is greater for ribbons than for chains when the oligomers are small. The difference is most significant for the dimers, decreasing as the oligomer grows. For the decamer (the largest oligomer considered) the order of stability reverses. Extrapolating this trend, we can expect the infinite chain to be more

Table 5.1. HF/D95** results for urea ribbons and chains. All values are given in kcal/mol. Total stabilization energy ΔE is uncorrected, last H-bond energy $\Delta E_n = \Delta E(n) - \Delta E(n-1)$ is given before and after counterpoise (CP) and zero-point vibrational (ZPVE) correction is applied. Values in parenthesis correspond to completely optimized oligomers, ZPVE correction values for n=5-10 are estimated, asymptotic values obtained by extrapolation using formula $E_n = E_2 + a \cdot (exp(b \cdot (2-n)) - 1)$.

n	ΔE	ΔE_n	CP	ZPVE	ΔE_n,CP	ΔE_n,ZPVE	ΔE_n,CP+ZPVE
ribbons							
2	-12.44	-12.44 (-12.75)	0.95	(1.92)	-11.49	-10.52	-9.57
3	-23.62	-11.18 (-11.37)	2.03	(3.63)	-10.10	-9.48	-8.40
4	-35.18	-11.56 (-11.65)	3.02	(5.37)	-10.57	-9.82	-8.38
5	-46.67	-11.49	4.04	7.08	-10.46	-9.78	-8.75
6	-58.23	-11.56	5.06	8.85	-10.54	-9.79	-8.77
7	-69.76	-11.54	6.08	10.62	-10.52	-9.77	-8.75
8	-81.32	-11.56	7.10	12.39	-10.54	-9.79	-8.77
9	-92.88	-11.55	8.13	14.16	-10.53	-9.78	-8.76
10	-104.44	-11.56	9.14	15.93	-10.55	-9.79	-8.78
∞		-11.58			-10.65	-9.81	-8.91
1D					-10.62		-8.88
chains							
2	-8.64	-8.64 (-8.78)	0.69	(1.06)	-7.96	-7.58	-6.90
3	-19.54	-10.89 (-11.01)	1.45	(2.08)	-10.13	-9.74	-8.97
4	-31.23	-11.69 (-11.79)	2.15	(3.36)	-11.00	-10.41	-9.71
5	-43.27	-12.04	3.06	4.80	-11.13	-10.60	-9.69
6	-55.49	-12.22	3.88	6.00	-11.41	-11.02	-10.21
7	-67.82	-12.33	4.69	7.20	-11.52	-11.13	-10.32
8	-80.22	-12.40	5.52	8.40	-11.57	-11.20	-10.37
9	-92.66	-12.44	6.34	9.60	-11.62	-11.24	-10.42
10	-105.14	-12.47	7.17	10.80	-11.65	-11.27	-10.45
∞		-12.49			-11.77	-11.38	-10.70
1D					-11.65		-10.58

stable than the infinite ribbon.

To analyze individual H-bonds, we used the last H-bond energy, ΔE_n, defined as the difference between stabilization for oligomers with *n* and *(n-1)* molecules. This value converges to the same asymptotic limit as the average H-bond energy. However, the convergence is faster, and thus, easier to extrapolate. After the pentamer the last H-bonding energy is stable within 0.1 kcal/mol for both chains and ribbons. This is in contrast with literature data for formamide, discussed previously in Section 2.4.

Table 5.1 indicates the last H-bond to be stronger for chains than for ribbons

starting with tetramer. Application of CP and especially ZPVE corrections favors

the chains, moving the crossover point to the trimers. For the chains the increase in the

magnitude of ΔE_n, is monotonic with the growth of the cluster. This behavior is

consistent with the chain structure which has only one repeating unit (Figure 5.1).

However, the magnitude of ΔE_n, oscillates for ribbons: decreasing with n for odd

oligomers, and almost constant for even oligomers. Ribbons have a repeating unit that

contains two molecules (Figure 5.1) where 1-3 interactions should be destabilizing

(see below). Thus, aggregation is progressively stabilizing H-bonding for chains, but

not for ribbons. We extrapolated the last H-bond energy (for ribbons, only even

oligomers were used) applying the same relationship:

$$\Delta E_n = \Delta E_2 + a \cdot (exp(b \cdot (2-n)) - 1)$$

The asymptotic value of ΔE_n, for chains is about 1 kcal/mol more stable than the

corresponding value for ribbons, which is comparable to H-bonding energy for the

ribbon dimer (see Figure 5.2). CP and ZPVE corrections increase the energetic
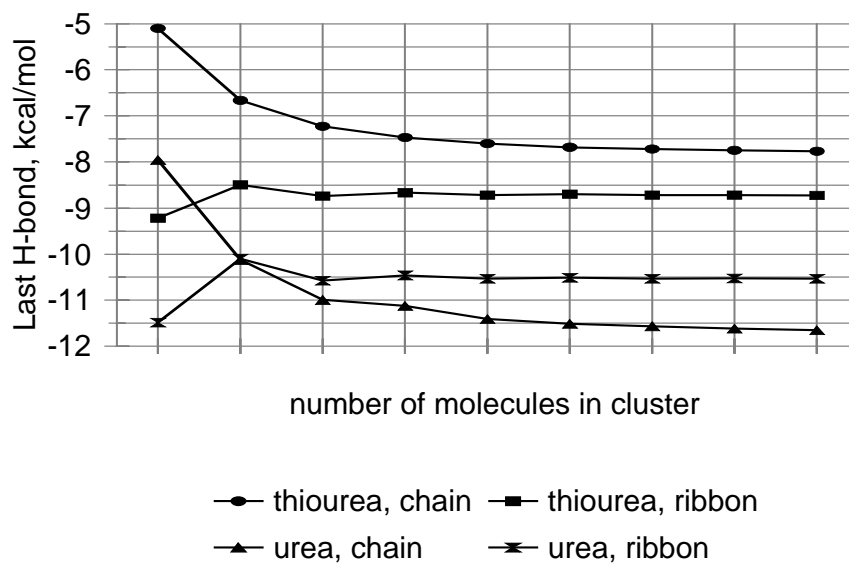
preference for the chain.

Figure 5.2. Comparison of last H-bond interaction energies, ΔE_n, urea and thiourea
chain and ribbon aggregates

Table 5.2. HF/D95** results on dipole moments μ(D), bond lengths (Å), and monomer deformation energies E_{def} (kcal/mol) for planar ribbons and chains of urea. Crystallographic values from neutron diffraction shown for comparison.

Ribbon								
1	C=O	C-N	N-Hs	N-Ha	O...H	μ		E_{def}
2	1.2047	1.3644	0.9911	0.9923		4.70		0.29
3	1.2164	1.3563	0.9997	0.9912	1.9856	0.00		0.48
4	1.2199	1.3543	0.9989	0.9912	1.9948	4.78		0.61
5	1.2218	1.3531	0.9998	0.9912	1.9943	0.00		0.69
6	1.2230	1.3525	1.0003	0.9912	1.9960	4.81		0.75
7	1.2238	1.3520	1.0007	0.9912	1.9958	0.00		0.80
8	1.2243	1.3517	1.0009	0.9912	1.9956	4.82		0.83
9	1.2248	1.3514	1.0011	0.9912	1.9954	0.00		0.86
10	1.2251	1.3512	1.0013	0.9912	1.9951	4.83		0.88
∞	1.2254	1.3511	1.0014	0.9912	1.9951	0.00		
	1.2259	1.3507	1.0018	0.9912	1.9919			
Chain								
1	C=O	C-N	N-Hs	N-Ha	O...H	μ/n	μ_n	E_{def}
2	1.2047	1.3644	0.9911	0.9923		4.70	4.70	0.12
3	1.2110	1.3595	0.9927	0.9919	2.2405	5.42	6.14	0.26
4	1.2146	1.3568	0.9938	0.9917	2.1894	5.82	6.62	0.38
5	1.2169	1.3551	0.9946	0.9915	2.1614	6.06	6.78	0.47
6	1.2184	1.3541	0.9952	0.9914	2.1440	6.22	6.86	0.54
7	1.2195	1.3533	0.9956	0.9914	2.1323	6.33	6.88	0.59
8	1.2204	1.3527	0.9959	0.9913	2.1239	6.41	6.88	0.64
9	1.2210	1.3523	0.9961	0.9914	2.1174	6.48	6.93	0.67
10	1.2215	1.3519	0.9963	0.9913	2.1126	6.53	6.93	0.70
∞	1.2220	1.3516	0.9964	0.9912	2.1087	6.57	6.93	
cryst	1.2233	1.3507	0.9967	0.9911	2.1002			
	1.2580	1.3440	1.0220	1.0040	2.001			

To evaluate the error in cluster calculations due to pseudoperiodical constraints we should compare constrained ΔE_n values from Table 5.1 with the totally optimized results (in parentheses). One can see, that the difference decreases from 0.3 kcal/mol in the ribbon dimer to 0.1 kcal/mol in both tetramers. Another possible cause for the errors in extrapolation of the cluster results to infinite systems is finite size of the system. The last H-bond energy values allow us to compare periodical and cluster calculation on chain and ribbon decamers. One can see, that difference between decamer and infinite structure (of the same molecular geometry) is small (0.07 kcal/mol) for ribbons and is absent for chains. The latter could be attributed to the

absence of geometric relaxation. Comparison with extrapolated value let us conclude that the presented scheme for extraction of intermolecular interaction from cluster calculations practically eliminates the errors due to finite cluster size. One can also note that chain termination error is significantly smaller than the geometry relaxation effect. This suggests the importance of geometry optimization for periodical calculations.

5.3 Comparison with previously published data

The results on interaction energies agree reasonably well with the results on dimers and trimers reported previously. Single-point HF calculations by Perez and Dupuis[1] in the custom basis set of DZ quality gave interaction energy of 12.4 kcal/mol and 27.8 kcal/mol for chain dimer and trimer (not accounted for the monomer relaxation and BSSE). Our values are lower: 8.6 and 19.5 kcal/mol (Table 5.1). For the interactions in the transverse trimer their value of 15.4 kcal/mol also exceeds 10.2 kcal/mol obtained in the present study.

A HF/6-31++G** value of 6.9 kcal/mol reported by Belosludov, Li, and Kawazoe[2] for the chain dimer (including molecular relaxation to nonplanar structure, but not CP correction), is in better agreement with our result of 6.2 kcal/mol (Table 4.8). Their value of interaction energy for the herringbone dimer is almost the same, compared to our value of 5.7 kcal/mol. For **CB** dimer they reported 9.0 kcal/mol, excellent agreement with the value of 9.0 in the present study (see Table 4.8). For the ribbon dimer and trimer their values (after CP correction) are 11.5, and 21.1 kcal/mol. If we subtract the planarization energy of 0.9 and 0 kcal/mol accordingly, the values (10.6 and 21.1 kcal/mol) are again in a good agreement with our values of 11.5 and

21.6 kcal/mol.

Our results disagree with conclusions by Belosludov, Li, and Kawazoe[2] about planarity of the ribbon trimer, based on frequency calculations at HF/6-31++G** level. Our full optimizations and frequency calculations on chain and ribbon clusters up to tetramers at HF/D95** level resulted in multiple imaginary frequencies (6 and 8 for ribbon trimer and tetramer, 8 and 9 for chain trimer and tetramer), proving the planar structure to be unstable. The biggest absolute values of imaginary frequencies correspond to piramidalization of NH_2 groups not involved in H-bonding and their values are close to those of the monomer. As we noticed in Chapter 4 for the urea monomer, increasing the size of the basis set tends to reduce the planarization barrier. However, planarization energies obtained by Belosludov, Li, and Kawazoe[2] for the monomer and the ribbon dimer (0.9 kcal/mol for both) exactly match our values.

We performed frequency calculations for the ribbon trimer at HF/6-31++G** level for fully optimized planar urea ribbon trimer. It yielded 4 imaginary frequencies. Therefore, planar conformation is not a minimum at this level of theory, and results reported by Belosludov, Li, and Kawazoe[2] are not confirmed.

5.4 Cooperative effects in chains and ribbons and pairwise decomposition

For chains the extrapolated value of ΔE_n is 46% greater than that of the chain dimer. For ribbons the extrapolated value of ΔE_n is 8% less than that of the dimer but very similar to ΔE_n, for the trimer and higher aggregates. The apparent anti-cooperative behavior of the ribbon is due to the repulsive nature of the 1-3 interactions

Table 5.3. Pairwise analysis HF/D95** results for urea chains and ribbons. All values are given in kcal/mol. Total stabilization energy: E_{DEF} molecular deformation in the cluster; Σpair - sum of pairwise interactions 12, 13, 14, and 15 taken m, l, k and j times accordingly to the number of the pairs in the cluster; ΔE_{NA} - difference between total stabilization for the cluster and Σpair.

n	E_{DEF}	m	ΔE_{12}	l	ΔE_{13}	k	ΔE_{14}	j	ΔE_{15}	Σpair	ΔE_{NA}
					Chains						
2	0.11	1	-8.19							-7.96	-0.00
3	0.26	2	-8.35	1	-0.88					-16.80	-1.29
4	0.38	3	-8.42	2	-0.91	1	-0.25			-25.82	-3.26
5	0.47	4	-8.46	3	-0.93	2	-0.25	1	-0.10	-33.90	-6.31
					Ribbons						
2	0.26	1	-12.01							-11.49	0.00
3	0.48	2	-12.32	1	1.37					-21.83	0.24
4	0.61	3	-12.51	2	1.37	1	-0.26			-32.50	0.34
5	0.69	4	-12.61	3	1.37	2	-0.26	1	0.12	-43.42	0.79

that do not exist in the dimer. To illustrate this point we calculated the pairwise components of the stabilization energies of the oligomers (Table 5.3). To this end, we performed single point CP-corrected calculations for all possible molecular pairs within the structure of the cluster. Interaction components for single molecules and molecular pairs are listed in the Table 5.2 along with the number of those components present in the total sum. The interaction for 1-2 pair is attractive (-12.3 to -12.6 kcal/mol), and for the 1-3 pair is repulsive (1.37 kcal/mol). The ratio of 1-2 to 1-3 interactions decreases from 2 (for the trimer) to 1 (for an infinite chain) as the aggregate grows. This is the primary reason for non-monotonic behavior of the last H-bond in the ribbons. All dimeric interactions within the chain are attractive, which is why the stabilization is monotonic with the cluster size.

As one can see from the Table 5.3, the total interaction energy is not the sum of 1- and 2-body interactions (i.e. monomer deformation and pairwise stabilization). This is because in the dimeric pairs molecular polarization differs from that in a cluster. We can see that a non-additive component is negative for the chains, and

slightly positive for the ribbons. In the ribbon dimer **AB** molecule **B** polarizes the molecule **A** in the direction AB. In the trimer **CAB** molecule **C** polarizes the molecule **A** in the opposite direction. As a result, interaction between **A** and **B** is not as attractive, as in the dimer. This results in destabilization of the trimer relative to the sum of dimeric interactions.

The dipole moment of the aggregates is also non-additive (is not equal to the vector sum of the monomers). The average dipole moment/molecule is increasing as a function of size (Table 5.3). For the urea chain, the dipole moment/molecule increases from the monomeric value of 4.70 D to 6.57 D in the decamer, an increase of 40%. Thus, the molecules become increasingly polarized as the chain grows. For the ribbon, the situation is quite different. All aggregates that contain even number of monomers have zero dipole moments because they are centrosymmetric. The dipole moments of the aggregates that contain odd quantities of monomers increase only modestly from 4.70 D in the monomer to 4.83 D in the nonamer. This behavior is consistent with a negligible level of non-additive component for the ribbons stabilization energy.

The results of the MP2, DFT and semiempirical calculations are qualitatively similar to the HF calculations discussed above. Table 5.4 indicates that the chain

Table 5.4. MP2/D95** results for urea ribbons and chains. See Table 5.1 for explanations. HF/D95** values were used for ZPVE corrections.

n	Ribbons					
	ΔE	ΔE_n	CP	ΔE_n, CP	ΔE_n, ZPVE	ΔE_n, CP+ZPVE
2	-15.86	-15.86	3.87	-12.00	-14.23	-10.36
3	-30.95	-15.08	7.62	-11.33	-13.64	-9.89
4	-46.41	-15.46	11.44	-11.64	-13.99	-10.16
5	-61.85	-15.44	15.28	-11.60	-13.99	-10.15
ext		-15.48		-11.66	-13.99	-10.17
	chains					
2	-10.41	-10.41	2.59	-7.81	-9.32	-6.73
3	-23.41	-13.00	5.31	-10.28	-11.95	-9.24
4	-37.36	-13.95	8.14	-11.12	-12.64	-9.81
5	-51.75	-14.39	11.04	-11.50	-12.92	-10.03
ext		-14.50		-11.55	-13.00	-10.05

dimer is 4% less stable, while the ribbon dimer is 4% more stable at the

MP2/D95** level than at HF/D95** level (after all corrections). Consequently, $\Delta E_{n,}$

for the chain tetramer does not exceed that for the ribbon tetramer (as it did for HF).

However, the extrapolated values suggest that $\Delta E_{n,}$ for the chain will exceed that for

the ribbons at some later point in the growth of the aggregates. The DFT results

reported in Table 5.5 are very similar to MP2. Although the stabilization energies and

CP-corrected ΔE_n for the ribbons are more negative than those for the chains even for

the decamer, this is not true after ZPVE correction. This result must be qualified since

ZPVE correction is extrapolated from the HF results for the tetramers. The AM1 and

SAM1 semiempirical calculation results are presented in Table 5.6. These are close to

the DFT results prior to ZPVE correction, which predict ribbons to be more stable.

Table 5.5. B3PW91/D95** results for urea ribbons and chains.

		Ribbons				
n	μ	ΔE	ΔE_n	ΔE_n, CP	ΔE_n, ZPVE	ΔE_n, CP+ZPVE
1	4.43					
2	0.00	-14.38	-14.38	-12.83	-12.46	-10.91
3	4.53	-27.60	-13.22	-11.64	-11.52	-9.94
4	0.00	-41.24	-13.64	-12.03	-11.90	-10.29
5	4.56	-54.85	-13.60	-11.99	-11.89	-10.28
6	0.00	-68.53	-13.69	-12.08	-11.92	-10.31
7	4.58	-82.21	-13.68	-12.06	-11.91	-10.29
8	0.00	-95.92	-13.71	-12.09	-11.94	-10.32
9	4.59	-109.63	-13.71	-12.09	-11.94	-10.32
10	0.00	-123.35	-13.72	-12.10	-11.95	-10.33
ext	4.61		-13.73	-12.11	-11.96	-10.34
		chains				
1	4.43					
2	5.31	-8.51	-8.51	-7.23	-7.59	-6.31
3	5.83	-19.69	-11.18	-9.74	-10.03	-8.59
4	6.15	-31.90	-12.21	-10.71	-10.93	-9.43
5	6.37	-44.59	-12.69	-11.16	-11.25	-9.72
6	6.54	-57.53	-12.94	-11.39	-11.74	-10.19
7	6.66	-70.63	-13.10	-11.53	-11.90	-10.33
8	6.76	-83.82	-13.19	-11.63	-11.99	-10.43
9	6.84	-97.08	-13.26	-11.67	-12.06	-10.47
10	6.89	-110.38	-13.30	-11.75	-12.10	-10.55
ext	7.07		-13.34	-11.77	-12.12	-10.57

Table 5.6. Semiempirical results for urea ribbons and chains. Energies are in kcal/mol, dipole moments in D.

	ribbons				chains		
n	μ	ΔE	ΔE_n		μ/n	ΔE	ΔE_n
	AM1					AM1	
1	4.14				4.14		
2	0.00	-8.80	-8.80		4.60	-6.13	-6.13
3	4.13	-17.02	-8.22		4.85	-13.54	-7.40
4	0.00	-25.41	-8.39		4.99	-21.38	-7.84
5	4.14	-33.75	-8.34		5.08	-29.40	-8.03
6	0.00	-42.13	-8.38		5.15	-37.53	-8.12
7	4.14	-50.49	-8.36		5.20	-45.70	-8.18
8	0.00	-58.87	-8.38		5.24	-53.91	-8.21
9	4.15	-67.24	-8.37		5.27	-62.15	-8.23
10	0.00	-75.61	-8.37		5.29	-70.39	-8.25
∞	4.15		-8.37		5.35		-8.27
	SAM1					SAM1	
1	4.23				4.23		
2	0.00	-8.04	-8.04		4.79	-3.85	-3.85
3	4.25	-15.41	-7.37		5.10	-9.33	-5.48
4	0.00	-23.10	-7.69		5.28	-15.40	-6.06
5	4.27	-30.72	-7.62		5.40	-21.72	-6.33
6	0.00	-38.40	-7.68		5.49	-28.18	-6.46
7	4.28	-46.07	-7.66		5.56	-34.72	-6.54
8	0.00	-53.76	-7.69		5.61	-41.31	-6.59
9	4.29	-61.43	-7.68		5.65	-47.93	-6.62
10	0.00	-69.11	-7.68		5.68	-54.57	-6.64
∞	4.32		-7.68		5.71		-6.67

5.5 Cooperative effects in transverse chains

Let us consider now transverse chains (Table 5.7). In the dimer (**AD** on Figure 3.4) one molecule **A** is H-donor, and molecule **D** is H-acceptor. Since permanent dipole moments of the molecules are antiparallel, the dipole moment of the dimer is due to the H-bond. Components of the dipole moment in the chain direction X and in the direction Z parallel to C=O bond are presented in Table 5.7. There are 2 types of transverse trimers: **EAD** and **GAF** on Figure 3.4. In **EAD** the central molecule is a donor of two H-bonds, and in **GAF** it accepts two H-bonds. Accordingly, the Z-

Table 5.7. HF/D95** results urea transverse chains. Energies are in kcal/mol, dipole moments are in D. See text for explanations.

n	ΔE	ΔE_n	ΔE_n,cp	ΔE_n,zpve	ΔE_n,cp+zpve	μ_x	μ_z	μ_z/mol	μ_{Hb}	μ_{nHb}
1							4.430	4.430		
2	-5.67	-5.67	-5.09	-4.77	-4.19	0.485	0.435		0.485	0.485
3	-10.18	-4.50	-4.00	-3.66	-3.16		5.496	4.705	0.791	0.306
3	-10.55	-4.88	-4.68	-4.04	-3.84		3.915			
4	-15.34	-5.16	-4.59	-4.32	-3.75	0.502	1.171		1.171	0.380
5	-20.00	-4.67	-4.15	-3.82	-3.31		6.250	4.711	1.539	0.369
5	-20.43	-5.10	-4.52	-4.25	-3.68		3.171			
6	-25.15	-5.15	-4.57	-4.30	-3.73	0.506	1.914		1.914	0.375
7	-29.84	-4.69	-4.17	-3.84	-3.33		7.000	4.715	2.285	0.371
7	-30.28	-5.13	-4.55	-4.29	-3.71		2.431			
8	-34.98	-5.15	-4.57	-4.30	-3.72	0.508	2.659		2.659	0.374
9	-39.67	-4.69	-4.19	-3.85	-3.34		7.745	4.717	3.028	0.368
9	-40.12	-5.14	-4.57	-4.30	-3.73		1.689			
10	-44.82	-5.15	-4.56	-4.30	-3.72	0.508	3.402		3.402	0.374

components of the dipole moments due to these H-bonds are parallel and antiparallel to the total dipole moment of the trimer, and X-componets cancel each other. Similar sinpolar and antipolar isomers exist for all the clusters with an odd number of molecules. The value for the dipole moment averaged over these isomers (μ_z/mol) corresponds to the dipole moment of one monomer, since Z-components of the dipole moment due to H-bonds cancel each other. This value shows a 6% increase from the monomeric dipole moment and does not significantly change with the cluster size. We can define the dipole moment due to one H-bond (μ_{Hb}) as the difference between μ_z/mol and the actual dipole moment. In the even cluster the whole value of Z-component of the dipole moment is due to one H-bond, as molecular dipole moments cancel each other.

The increment of μ_{Hb} after addition of one new H-bond (μ_{nHb}) is also listed in Table 5.7. It is decreasing for even clusters (from 0.49 D for the dimer) and increasing for odd clusters (from 0.31 D for the timer) to the same asymptotic value of 0.37 D). The energy of the last H-bond displays similar behavior. Like in the ribbons, H-bond

is the strongest for the dimer (4.2 kcal/mol after CP and ZPVE corrections), and

the weakest for the trimer (3.2 kcal/mol). As the cluster grows, the value decreases for

even clusters, and increases for odd clusters, converging around 3.7 kcal/mol. Both

possible conformers of odd clusters have weaker H-bonds then even clusters.

5.6 Chains and ribbons of the thiourea

The results of similar calculations of ribbons and chains formed by thiourea are

presented in Tables 5.8. Ribbons are predicted to be more stable than chains for all

aggregates (independent of size) at both HF and DFT levels. No MP2 calculations

were performed for the thiourea aggregates due to the limitations of our computational

resources. The interaction energies between thiourea molecules are significantly less

than between urea molecules. Furthermore, the ratio of the interaction energies in the

chain vs. ribbon dimers is 0.55 for the thiourea compared to 0.72 for the urea

(HF/D95**). While the cooperative effect upon the extrapolated value of the thiourea

chain for the infinite chain is comparable to that for urea, 53% vs. 55% (HF/D95**), it

is insufficient to overcome the more favorable interaction energy of the chain

compared to the ribbon dimer. Figure 5.2 presents a comparison of urea and thiourea

CP-corrected ΔE_n's in chains and ribbons.

The dipole moments of the thiourea chain increase from the monomeric value

of 5.95 to 7.96 D in the decamer, an increase of 36% (similar to the 40% increase for

urea). For the ribbon, the nonamer has a dipole moment of 6.13 D, only slightly more

than the monomeric value of 5.96 D.

Table 5.8. Ab initio results for thiourea ribbons and chains. Energies are in kcal/mol, dipole moments in D.

	Ribbons					chains			
N	μ	ΔE	ΔE_n	ΔE_n, CP		μ/n	ΔE	ΔE_n	ΔE_n, CP
					HF/D95**				
1	5.95					5.95			
2	0.00	-10.67	-10.67	-9.22		6.73	-5.42	-5.42	-5.10
3	6.08	-20.59	-9.92	-8.50		7.15	-12.45	-7.03	-6.66
4	0.00	-30.76	-10.17	-8.74		7.41	-20.05	-7.61	-7.23
5	6.11	-40.87	-10.11	-8.67		7.58	-27.92	-7.86	-7.47
6	0.00	-51.04	-10.16	-8.72		7.70	-35.91	-8.00	-7.60
7	6.12	-61.18	-10.15	-8.70		7.79	-43.99	-8.07	-7.68
8	0.00	-71.35	-10.17	-8.72		7.86	-52.11	-8.12	-7.72
9	6.13	-81.51	-10.16	-8.72		7.92	-60.26	-8.15	-7.75
10	0.00	-91.67	-10.17	-8.73		7.96	-68.43	-8.17	-7.77
∞	6.14		-10.17	-8.73		8.11		-8.19	-7.79
					B3PW91/D95**				
1	5.43					5.43			
2	0.00	-11.91	-11.91	-10.38		6.38	-5.19	-5.19	-4.78
3	5.60	-23.08	-11.17	-9.66		6.92	-12.25	-7.06	-6.59
4	0.00	-34.53	-11.45	-9.91		7.27	-20.05	-7.79	-7.28
5	5.63	-45.94	-11.41	-9.87		7.50	-28.17	-8.13	-7.61
6	0.00	-57.42	-11.48	-9.95		7.68	-36.48	-8.30	-7.76
7	5.64	-68.86	-11.44	-9.89		7.80	-44.74	-8.26	-7.71
8	0.00	-80.34	-11.48	-9.93		7.90	-53.36	-8.62	-8.07
9	5.65	-91.81	-11.47	-9.92		7.98	-61.87	-8.51	-7.96
10	0.00	-103.29	-11.48	-9.93		8.04	-70.42	-8.54	-7.99
∞	5.64		-11.48	-9.93		8.10		-8.57	-8.02

5.7 Simulations of intermolecular interactions using a uniform electric field

In the chain cluster considered in this chapter all molecular dipole moments are aligned in parallel. Therefore, an external field exerted upon one of the central molecules of the cluster by its neighbors is expected to be rather uniform. This opens up an opportunity to compare the effect of purely electrostatic interactions with the total effect of intermolecular interaction on atomic and electronic structure of the molecule. To perform this comparison we completed geometry optimization on planar

Table 5.9. HF/D95** results for urea monomer and chain dimer in a uniform electric field F (a.u.): dipole moment μ (D), stabilization energy ΔE (kcal/mol), classical stabilization energy μF (kcal/mol), and bond lengths (Å). Available values for the chain decamer, and experimental values are shown for comparison.

F	μ/mol	ΔE	μ F	H...O	C=O	C-N	N-Ha						
	chain monomer												
0.00	4.70	0.00	0.00		1.205	1.364	0.991						
0.01	5.61	-12.74	-13.86		1.216	1.357	0.993						
0.02	6.52	-27.72	-32.21		1.229	1.351	0.996						
0.03	7.44	-44.95	-55.08		1.243	1.345	1.000						
0.04	8.36	-64.45	-82.52		1.259	1.339	1.004						
0.05	9.29	-86.23	-114.65		1.276	1.334	1.009						
	chain dimer				Average			H-donor monomer			H-acceptor monomer		
0.00	5.45	-8.84	0.00	2.222	1.211	1.359	0.993	1.210	1.361	0.994	1.212	1.357	0.991
0.01	6.29	-12.37	-15.53	2.118	1.225	1.351	0.997	1.223	1.354	0.999	1.228	1.348	0.994
0.02	7.11	-18.33	-35.13	2.020	1.241	1.344	1.002	1.238	1.347	1.007	1.245	1.340	0.998
0.03	7.93	-24.95	-58.74	1.924	1.260	1.337	1.009	1.255	1.341	1.017	1.265	1.333	1.002
0.04	8.75	-33.25	-86.37	1.825	1.281	1.330	1.020	1.275	1.335	1.033	1.288	1.325	1.007
0.05	9.56	-43.81	-118.06	1.710	1.307	1.324	1.036	1.298	1.330	1.059	1.316	1.318	1.014
MW	3.83	0.00			1.221	1.378	0.998						
crystal	4.66	-21.00		2.062	1.265	1.349	1.008						
decamer	6.93	-11.65		2.109	1.222	1.352	0.996						

urea monomers and chain dimers in a uniform electric field of different strength. The results are reported in Table 5.9 and Figure 5.3.

One can see that classical electrostatic stabilization of the dipole in a field is close to HF stabilization energy of the molecule in the field. The values of the dipole moment, stabilization energy and C-N, C=O and N-H covalent bond lengths in the monomer change to their respective values in the decamer (marked by horizontal lines on Figure 5.3) in rather narrow range of an external field 0.015-0.022 a.u. The stabilization that corresponds to an infinite chain of H-bonding urea molecules occurs at an applied field of 0.016 a.u., dipole moment and C=O bond length attains the infinite chain value at the same value of an applied field, whereas C-N and N-H bonds attain the infinite chain value at 0.018 and 0.021 a.u., respectively. For the monomer a weaker field (about 0.01 a.u.) is necessary to achieve these values. This is expected, since a second monomer creates an additional field. H-bond length in the dimer also
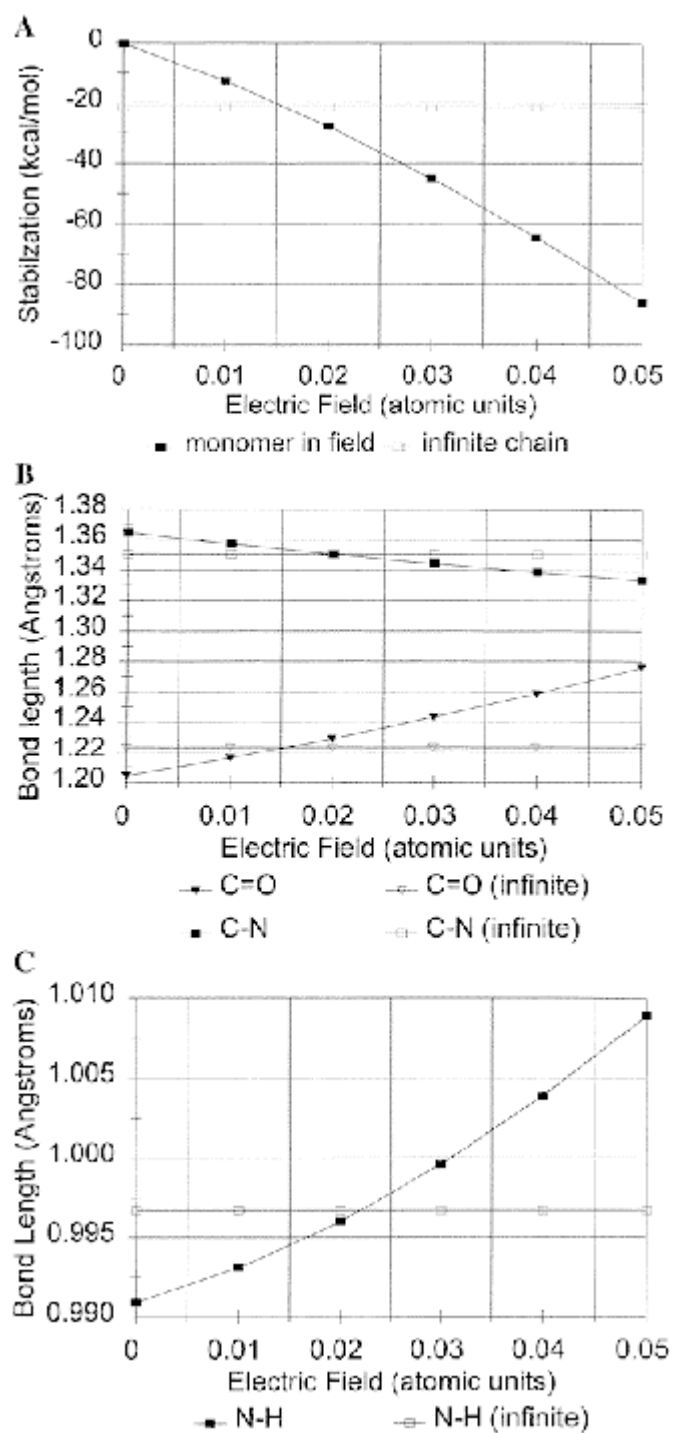
Figure 5.3. Urea in an electric field: (A) Stabilization energy; (B) C=O and C-N bond lengths; (C) N-H bond length. The unfilled markers that form the horizontal lines indicate extrapolated values for infinite H-bonding chains at the HF/D95** level.

follows this trend.

To apply a similar approach to another system, we compared HF/D95** results on an H-bonded chain of 1,3-pentenedione molecules (Figure 5.4) to the monomer in the uniform field (Table 5.10, and Figure 5.5). This system is simulating crystalline 1,3-cyclohexanedione, (Figure 5.4) studied previously.[3]

This time one can see the striking difference. An applied field of about 0.012 au corresponds to the stabilization of an infinite chain. The C=C and C=O bond lengths reach the infinite chain values at applied fields of 0.008 and 0.007 a.u., respectively, whereas the C-C and C-O bonds reach the corresponding values at applied fields of 0.020 and 0.021 au, respectively. The value of the applied electric field which reproduces the stabilization of an individual molecule as calculated in an infinite hydrogen-bonding chain (0.008 au) is very different from that needed to reproduce the changes of the dipole (0.018 au), and most of the geometric parameters (C-C and C-O bond lengths). Fields of 0.007 to 0.021 au are needed to reproduce all of the infinite chain data for 1,3-propanedione. This range of fields is almost three times that calculated for urea. Thus, the hydrogen bonds in the infinite chains of urea and 1,3-propanedione seem to fall into distinctly different categories.
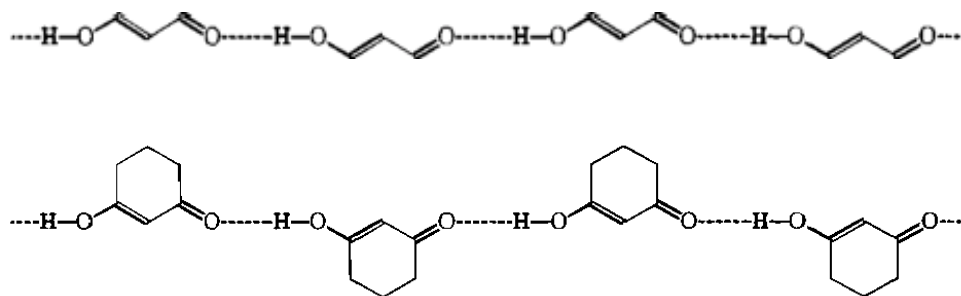

Figure 5.4. H-bonded chain of 1,3-propanedione molecules (top) simulating the chain in crystal structure of 1,3-cyclohexanedione (bottom)
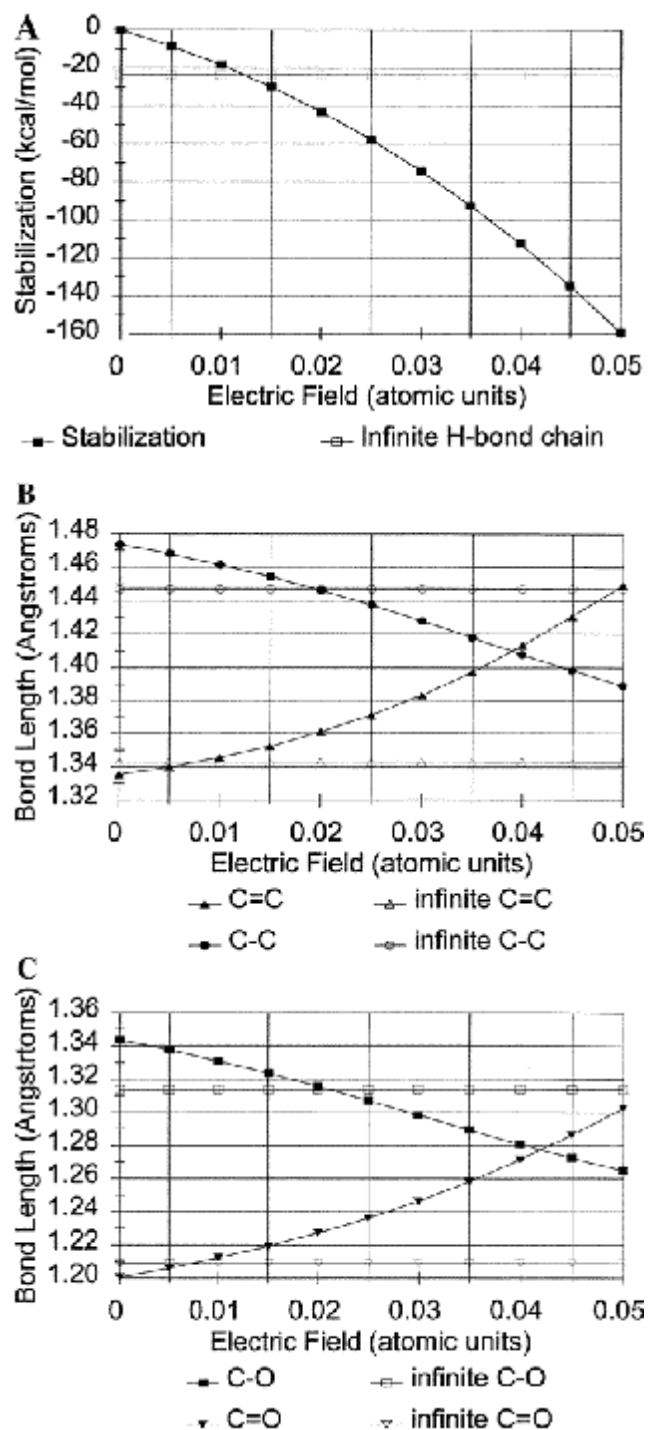
Figure 5.5. Enol of 1,3-propanedione in an electric field. (A) Stabilization energy (equivalent to H-bonds at each end); (B) C-C and C=C bond lengths; (C) C-C and C=C bond lengths. The unfilled markers indicate extrapolated values for infinite H-bonding chains at the HF/D95** level.

Table 5.10. HF/D95** results for monomer and dimer of 1,3-pentenedione in a uniform electric field F (a.u.), compared to chains up to octamer: dipole moment μ (D), stabilization energy ΔE (kcal/mol), and bond lengths (Å).

N	O...O	C=O	C-C	C=C	C-O	O-H	ΔE_n	ΔE_n,cp	ΔE_n,cp+zpve	μ_n	μ
1	-	1.195	1.469	1.330	1.338	0.943				5.62	5.62
2	2.812	1.201	1.461	1.335	1.328	0.948	-9.90	-9.32	-8.02	7.60	13.22
3	2.775	1.204	1.456	1.338	1.323	0.951	-11.86	-11.19	-9.89	8.72	21.94
4	2.754	1.205	1.453	1.339	1.320	0.952	-12.51	-11.81	-10.51	8.86	30.80
5	2.741	1.207	1.451	1.341	1.318	0.954	-12.80	-12.09	-10.79	9.00	39.80
6	2.734	1.208	1.450	1.341	1.316	0.954	-12.94	-12.24	-10.94	9.03	48.83
7	2.727	1.208	1.449	1.342	1.315	0.955	-13.04	-12.37	-11.07	9.09	57.92
8	2.722	1.209	1.448	1.343	1.314	0.956	-13.09	-12.42	-11.12	9.11	67.03
∞	2.694	1.209	1.447	1.343	1.314	0.956		-13.11	-11.81		
F	dimer	monomer									
0.000	2.811	1.195	1.469	1.330	1.338		0.00			5.62	
0.005	2.731	1.201	1.463	1.335	1.329		-7.52			6.58	
0.010	2.640	1.206	1.455	1.341	1.321		-16.26			7.58	
0.015	2.539	1.213	1.447	1.348	1.311		-26.26			8.64	
0.020	2.449	1.221	1.438	1.357	1.302		-37.61			9.77	
0.025		1.230	1.429	1.368	1.292		-50.40			10.97	
0.030		1.241	1.419	1.381	1.282		-64.73			12.27	
0.035		1.253	1.408	1.396	1.272		-80.71			13.64	
0.040		1.267	1.398	1.414	1.262		-98.44			15.09	
0.045		1.283	1.389	1.433	1.253		-117.99			16.60	
0.050		1.300	1.381	1.455	1.245		-139.43			18.13	

We can intrpret this difference as being due to the increased covalent character of H-bonding in 1,3-propanedione than in urea. H-bonds in the former are symmetric in the sense that concerted hydrogen transfer from the donor to the acceptor in the infinite chain results in the identical state of the system.

The dimer calculations show that an external field is necessary to bring the H-bond length to that of the infinite chain is 0.008 au. At the strength of the filed of 0.018 au the hydrogen is transferred from the donor to the acceptor molecule. Increase in the field strength over 0.019 a.u. breaks the H-bond and pulls the ionic pair apart (Figure 5.6). Similar results on external electric field initiating proton transfer,[4] and other chemical reactions[5] were reported previously. The trend toward equilization of the bond lengths in an external field also reported for H-bonded complexes,[6] as well as
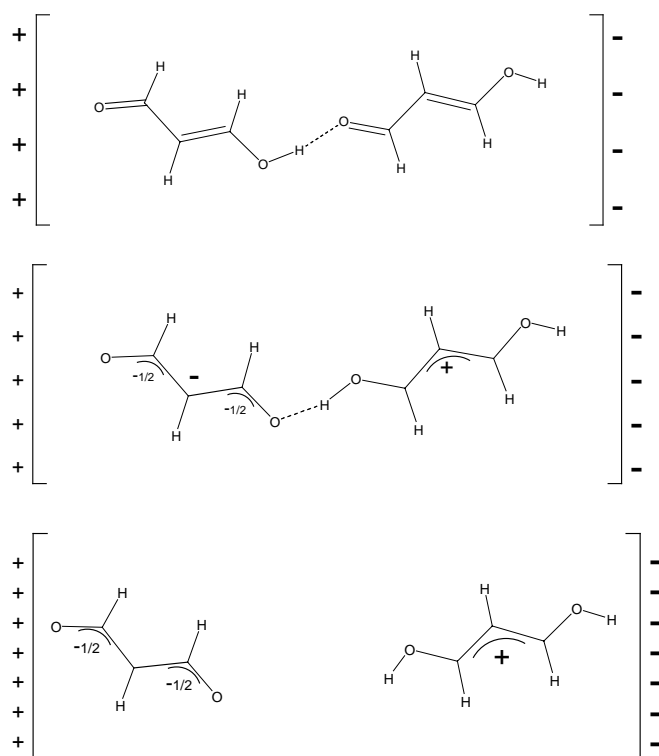
for conjugated molecules.[7]

Figure 5.6. The dimer of 1,3-propanedione in an electric field of 0.018 a.u. (top), 0.019 a.u. (middle), and 0.020 a.u. (bottom)

5.8 Conclusions

The observed differences in the hydrogen-bonding patterns within the crystal structures of the urea (which forms chains) and the thiourea (which forms ribbons) is primarily due to the relative quantitative strengths of the H-bonds in the relevant dimers. For both urea and thiourea, the ribbon dimer (which contains two H-bonds with each O or S acting as an acceptor) is more stable than the chain dimer (where one O or S is the acceptor for both H-bonds). The comparable interactions are weaker in the thiourea than in urea. Furthermore, the relative strength of the ribbon vs. the chain

is greater in the thiourea. The cooperative interactions for the urea and thiourea chains are similar. The cooperative interactions for both ribbons are negligible. The result is that, as the chains grow, the cooperative interaction of the urea chain (but not the thiourea chain) becomes sufficient to overcome the disparity between the H-bonding energies of the chain and ribbon dimers. Whereas relative cooperative stabilization for urea is even less than for the thiourea, the chain dimer for urea is only 44% less stable than the ribbon dimer, and chain dimer for thiourea is 81% less stable than the ribbon dimer. That inequality allows urea chains to become the most stable aggregate for larger clusters.

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